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 AUTHOR(S): FUTRELL, TL, GOODPASTURE, RT, LARSON, GF,
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 AUTHOR(S): WHITE, LE, CARTER JR, MH,
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 AUTHOR(S): NCELHANEY, RJ, MANN, ML,
 MISC: PRESENTED AT 24TH CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY, GATLINBURG, TN, OCT 7-9, 1980
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 AUTHOR(S): LARSON, GF, VIATOR, RA,
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DETERMINATION OF MERCURY IN ROCKS, SEDIMENTS,
AND SOILS BY FLAMELESS ATOMIC ABSORPTION

L. E. White
M. H. Carter, Jr.

May 1980

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Y/DK-254

DETERMINATION OF MERCURY IN ROCKS, SEDIMENTS, AND SOILS
BY FLAMELESS ATOMIC ABSORPTION

L. E. White
M. H. Carter, Jr.

Plant Laboratory Department
Y-12 Product Certification Division

Oak Ridge Y-12 Plant
P. O. Box Y, Oak Ridge, Tennessee 37830

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ABSTRACT

A simple, relatively fast method for the determination of mercury in rocks, sediments, and soils has been developed to meet the needs of the National Uranium Resources Evaluation Project(a).

One gram of the less than 100 mesh material is placed in a 250-mL reagent bottle and is digested using a mixture of concentrated sulfuric acid and 30% hydrogen peroxide. To prevent the loss of mercury during the digestion procedure, an 18-inch dry reflux tower is employed. After digestion, the sample is treated with a 5% potassium permanganate solution, and a sodium chloride-hydroxylamine sulfate reagent. Tin (II) sulfate is then added and the sample immediately attached to an aeration device. The volatilized mercury is swept into an absorption cell by an argon stream and is measured by an atomic absorption spectrophotometer adjusted to 253.7 nanometer wavelength. Absorption is then plotted by a strip chart recorder.

(a) Operated for the Department of Energy by Union Carbide Corporation's Nuclear Division.

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SUMMARY

A procedure for the determination of mercury in rocks, sediments, and soils has been developed. It involves a sulfuric acid and hydrogen peroxide digestion and subsequent reduction of mercury in the sample to the metallic vapor state which is swept by an argon stream into an absorption cell. The volatilized mercury is measured by an atomic absorption spectrophotometer adjusted to 253.7 nanometer absorption wavelength. Absorption is then plotted by a strip chart recorder. The procedure has an average throughput rate of 20 to 30 samples in an eight-hour period.

Analysis of the NBS SRM 1645 River Sediment certified for mercury to be 1.1 ± 0.5 ppm was 1.11 ± 0.26 ppm (44 determinations).

INTRODUCTION

The National Uranium Resources Evaluation Project required the development of a relatively fast procedure for the analysis of mercury in rocks, sediments, and soils. Many of these samples were unusually high in organic matter (10-30%). Since organic matter can lead to high and erroneous readings, a strong oxidation of the sample was required. A sulfuric acid and hydrogen peroxide digestion was chosen and after sample preparation, standard flameless atomic absorption spectroscopy was employed.

DETERMINATION OF MERCURY^{1,6}

APPARATUS

The determination of mercury by flameless atomic absorption spectroscopy is accomplished using the apparatus shown in Figure 1. The atomic absorption spectrophotometer being used must have an open burner area in which to mount an absorption cell. The cell measured 10 centimeters in length and 2 centimeters inside diameter with end windows constructed of quartz. Cell mounting could then be accomplished by strapping the absorption cell directly to the burner assembly.

Argon gas is passed through a flowmeter at a rate of 1 liter per minute to a set of 3-way bypass valves which direct the argon through a coarse straight glass frit for aeration of the sample during analysis or divert the argon directly to the absorption cell thereby establishing background. In both cases a drying tube (6-inch x 0.75-inch Pyrex) containing 20 grams of magnesium perchlorate is used prior to the absorption cell to remove all water vapor from the argon gas.

REAGENTS

All chemicals should be of reagent grade quality and low in mercury.

Hydrogen peroxide (H_2O_2), concentration (30%)

Nitric acid (HNO_3), 7 N solution

Potassium permanganate (KMnO_4), 5% solution, w/v

Sodium chloride-hydroxylamine sulfate [$\text{NaCl} - (\text{NH}_2\text{OH}) \cdot \text{H}_2\text{SO}_4$] solution: Dissolve 12 grams of NaCl and 12 grams of $(\text{NH}_2\text{OH}) \cdot \text{H}_2\text{SO}_4$ in 100 mL of water.

Tin (II) sulfate (SnSO_4) solution: Dissolve 50 grams of SnCl_2 in 100 mL of 10% H_2SO_4 , heat to 75°C if needed, and dilute to 500 mL with water. If a precipitate remains, simply assure a homogeneous suspension by frequent agitation during use.

Stock mercury solution, 1000 μg Hg/mL : Dissolve 0.1354 gram of mercury (II) chloride (HgCl_2) in 100 mL of 1 N sulfuric acid (H_2SO_4).

Working mercury solution, 1 μg Hg/mL : Dilute the 1000 μg Hg/mL stock solution 1:1000 with water. Prepare fresh daily.

Working mercury solution, 0.1 μg Hg/mL : Dilute the 1 μg Hg/mL working solution 1:10 with water. Prepare fresh daily.

Sulfuric acid, concentrated

Sulfuric acid, 10% solution

PROCEDURE

Instrumentation

Optimize the wavelength setting of the atomic absorption spectrophotometer using 253.7 nanometer mercury line, by preparing a 0.5 μg mercury standard, attaching the aerating apparatus, and adjusting the instrument wavelength

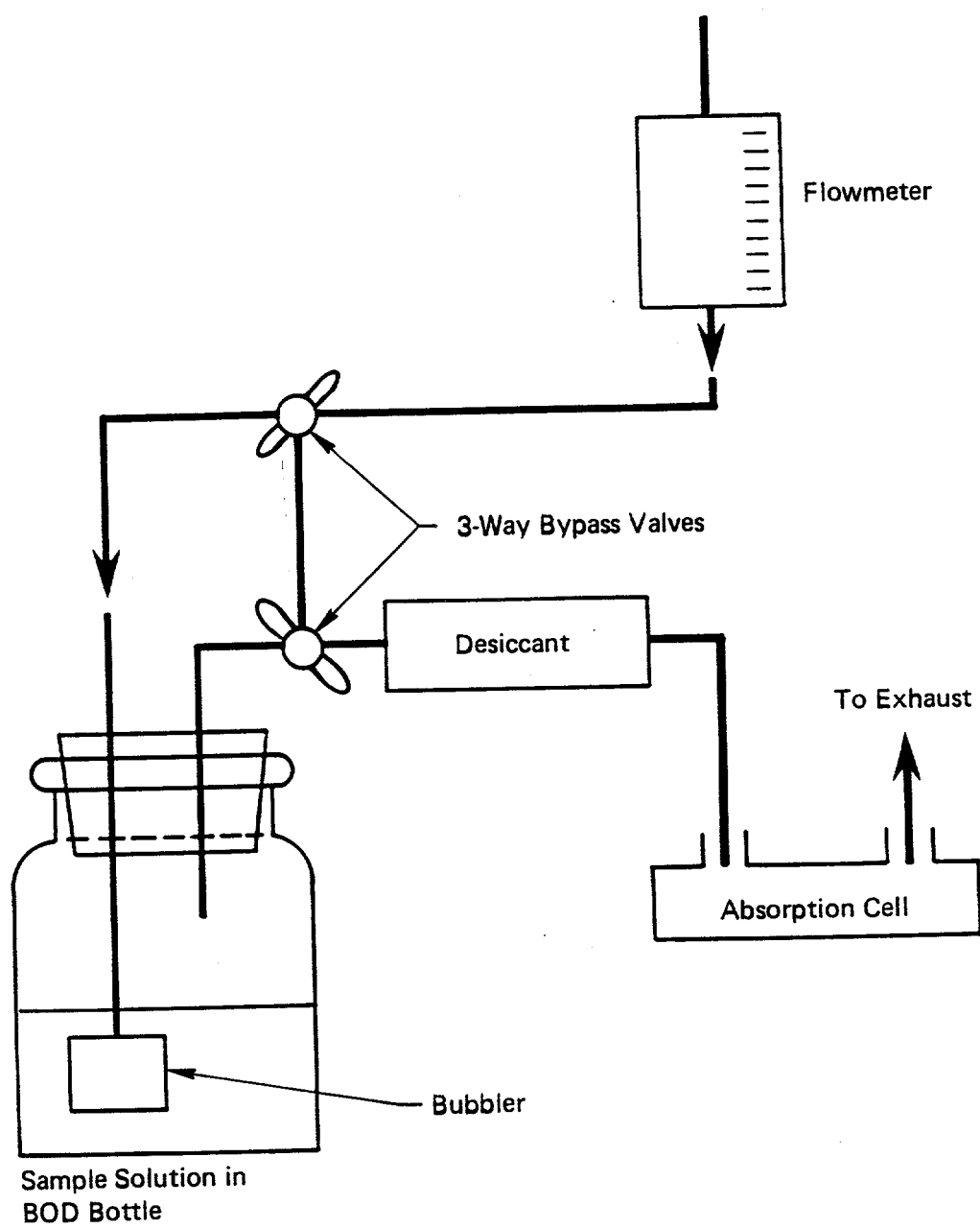


Figure 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION.2, 5

and expansion units.

Standard Preparation

1. Into clean 250-mL reagent bottles, pipette 1, 2, 3, 4, and 5 mL respectively of the 0.1 $\mu\text{g/mL}$ mercury working stock solution to make 0.1, 0.2, 0.3, 0.4, and 0.5 μg standards.
2. Make additions to each standard plus a reagent blank, 25 mL of concentrated sulfuric acid and 10 mL of 7 normal nitric acid.
3. Dilute with agitation to 100 mL with distilled water.
4. Attach an 18-inch dry reflux tower fabricated from 0.5-inch Pyrex tubing and a 19/40 ground glass joint. At this point carry the standards through the sample preparation procedure beginning with Step 4.

Sample Preparation

1. Weigh one gram of the less than 100 mesh rock, sediment, or soil into a clean 250-mL reagent bottle.
2. Add 25 mL of concentrated sulfuric acid to the sample. Swirl to completely wet the sample.
3. Carefully add with swirling three 1-mL portions of 30% hydrogen peroxide allowing sufficient time for the decomposition of peroxide between additions.
4. Place the samples and standards, both fitted with reflux towers, on a controllable hot plate starting at a temperature setting of 75°C (using a surface thermometer) and increase the temperature at 25°C increments and 15-minute intervals until a temperature of 150°C is attained. Allow the samples to remain at this temperature for 10 minutes. At this point, remove them from the heat and allow to cool.
5. While holding the sample bottle at a slight angle, rinse down the reflux tower with a minimum amount of water. Remove the tower.
6. Add, with swirling, 70 mL of distilled water.
7. Pipette 1 mL of 5% potassium permanganate solution into each sample and swirl to mix. If a permanent pink coloration is not obtained, make a second 1-mL addition of the reagent. If at this time the pink color is not permanent, replace the reflux tower and return to the hot plate for an additional 15 minutes. Repeat Step 7.
8. Pipette 1 mL of the sodium chloride-hydroxylamine sulfate reagent into the sample. With agitation, the pink coloration will disappear.
9. Pipette 4 mL of tin (II) sulfate into the sample. Immediately attach the

aeration apparatus.

10. Introduce argon through the sample and record the mercury peak. Channel B is operated at one-half the scale expansion of channel A. (See Figures 2 and 3.)

CALCULATIONS

1. Determination of Mercury From a Standard Curve

- a. Determine the peak heights of each of the standards used. Divide each standard concentration by the peak heights measured. Calculate an average factor from the results.
- b. Determine the peak height of the sample from the strip chart.
- c. Calculate the mercury concentration of the sample from:

$$H = \frac{S \times P}{G}$$

where: H = mercury concentration in ppm,
 S = standard factor,
 P = peak height of sample, and
 G = sample weight in grams.

2. An Alternate Method

- a. Determine the peak heights of the sample from the strip chart.
- b. Read the mercury concentration of the sample from the standard curve.
- c. Calculate the mercury concentration of the sample from:

$$H = \frac{M}{G}$$

where: H = mercury concentration in ppm,
 M = micrograms of mercury in sample solution, and
 G = sample weight in grams.

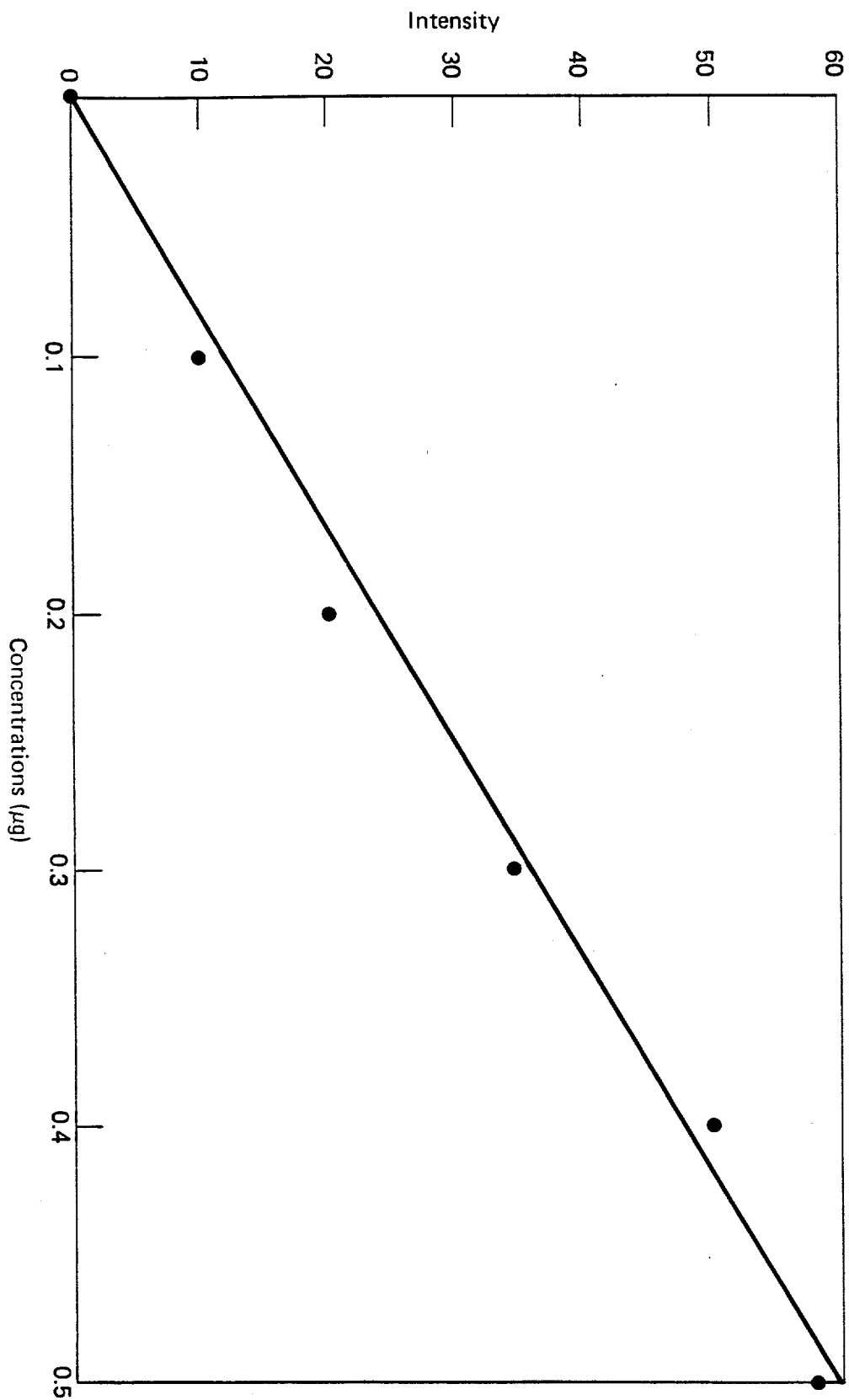
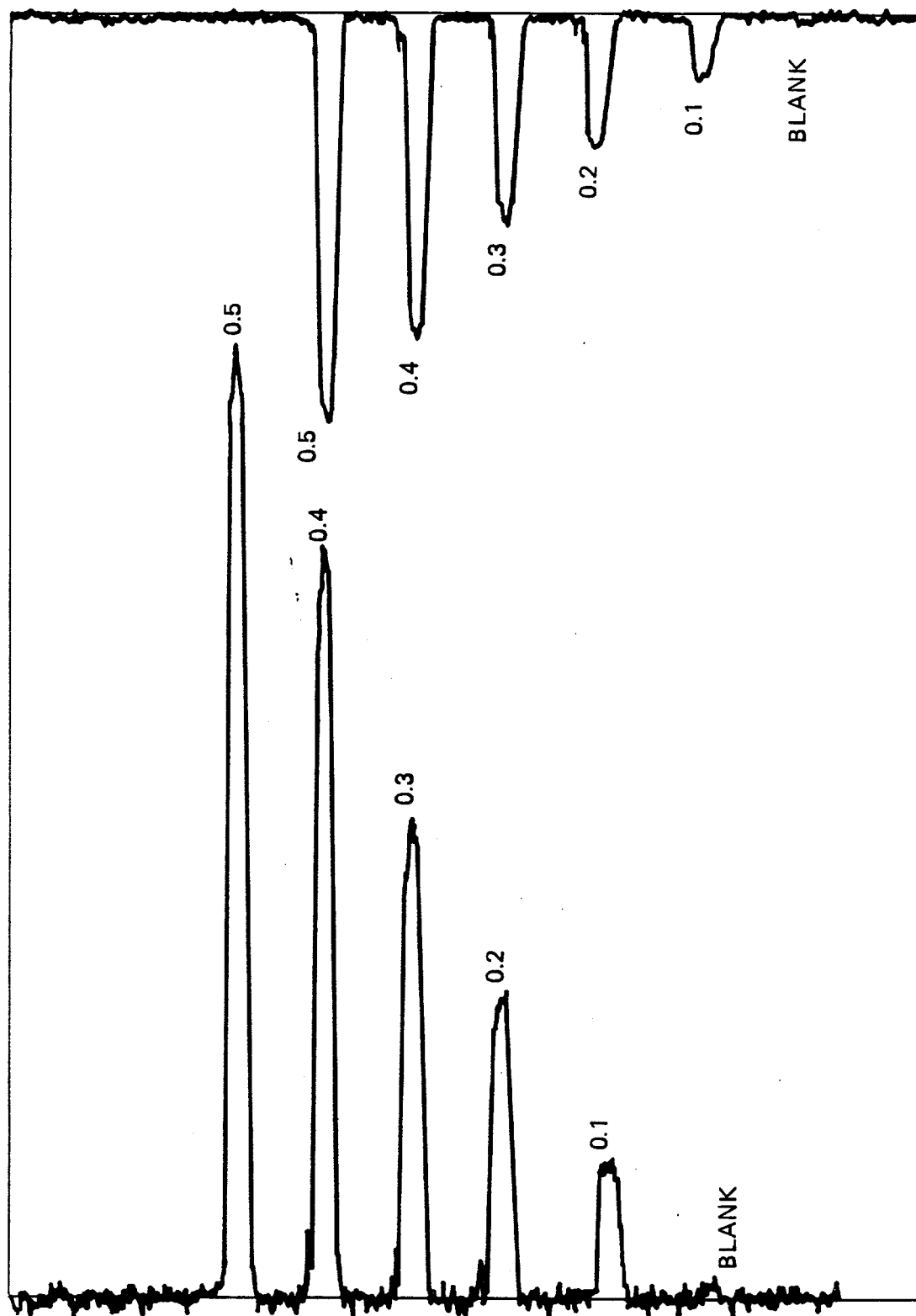


Figure 2. MERCURY CURVE (STANDARD CONCENTRATIONS (µg) VS RECORDER RESPONSE)



Channel A

Figure 3. STRIP CHART PRINT-OUT OF MERCURY STANDARDS

Channel B

DISCUSSION

The digestion procedure described is applicable to a variety of rock, sediment, and soil types. It is particularly useful where samples high in total carbon are to be analyzed. Since many organic species absorb in the region of the mercury wavelength, traces of organic material could cause erroneously high readings assumed to be due to mercury absorption. A very strong digestion procedure alleviates the problems with interferences from the organic matter.

When using the sulfuric acid, hydrogen peroxide digestion, it is necessary to heat the samples to a point where mercury retention is questionable. To prevent any volatilization, an 18-inch dry reflux tower is used during the heating process. This effectively stops any loss of mercury.

When used as described, this procedure is simple, accurate, and fast. Average throughput for one analyst is 20 to 30 samples per 8-hour day. Analysis of a NBS SRM certified to be 1.1 ± 0.5 ppm was 1.11 ± 0.26 ppm (on 44 determinations over a 2-month period by 5 analysts).

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